

- [54] DEVELOPER COMPOSITION FOR PRODUCING PHOTOGRAPHIC MATERIALS FOR THE GRAPHIC ARTS
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- [51] Int. Cl. **G03c 5/30**
- [58] Field of Search..... **96/66, 66.3, 107**

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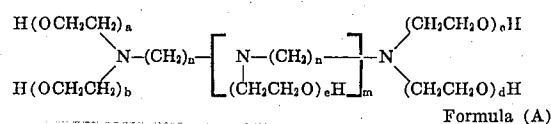
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Attorney, Agent, or Firm—Sughrue, Rothwell, Mion, Zinn & Macpeak

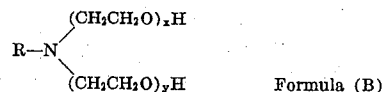
[57] ABSTRACT

A developer composition for producing photographic materials for the graphic arts comprising a dihydroxy benzene developing agent and at least one polyethoxy amino compound represented by the following formula A:



wherein n ranges from 2 to 10;
m ranges from 0 to 6; and $a + b + c + d + e \times m$
ranges from 5 to 200 with a, b, c, d and e each
representing an integer other than 0.

or the formula B



wherein R represents an alkyl group of less than four carbon atoms, where $C_4 x \times y$ ranges from 3 to 100 or R represents a $-(\text{CH}_2\text{CH}_2\text{O})_z\text{H}$ group, where $x + y + z$ ranges from 5 to 100, in which x, y and z each represent an integer other than 0 is disclosed.

20 Claims, No Drawings

DEVELOPER COMPOSITION FOR PRODUCING PHOTOGRAPHIC MATERIALS FOR THE GRAPHIC ARTS

BACKGROUND OF THE INVENTION

1. Field of the Invention

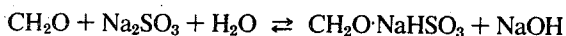
The present invention relates to a photographic developer composition for developing a high-contrast photographic element useful for the graphic arts.

2. Description of the Prior Art

Photographic line and halftone reproductions are carried out by imagewise exposing a high-contrast or litho-type silver halide photographic element through a cross hatch screen or contact screen and then developing it with a developer, whereby continuous tone images are converted into photographic line and halftone (dot) images.

It is most desirable that the line and dot images be composed of only a maximum density portion and a background having a minimum density. However, since a high-contrast photographic element has the property of forming an intermediate density portion in addition to a maximum density portion and background, a portion of intermediate density which is termed fringe is always formed around the dot images. The formation of fringe is not desirable for graphic arts because it is deteriorates the dot qualities.

As is well known in the art, the fringe can be removed by using a so-called infectious developer composition which essentially contains a dihydroxybenzene type developing agent and a small amount of sulfite ion. In a conventional developer composition, a dihydroxybenzene type developing agent, for example, hydroquinone is converted into quinone during the development process and the resulting quinone reacts with sodium sulfite to produce sodium hydroquinonemonosulfonate. However, sodium hydroquinonemonosulfonate is less reductive than hydroquinone due to its low electrode potential, and therefore is almost incapable of acting as a developing agent. Accordingly, the progress of development is not conducted rapidly, thus a fringe is formed. In contrast to this, where an infectious developer composition is used, the concentration of free sulfite ions is maintained at a low concentration, since sodium sulfite is added in a small amount and since it reacts with a compound having carbonyl groups, such as para-formaldehyde, incorporated in the infectious developer composition, in accordance with the following equation:



For this reason, in the development process it becomes difficult for the quinone to react with sulfurous acid to produce hydroquinonemonosulfonic acid, and thereby the concentration of quinone is increased. The thus produced quinone and the original hydroquinone cause a disproportionation reaction and produce semiquinone. The semiquinone reduces silver halide and itself is converted to quinone due to its high developing activity. The description by Yule in *J. Frank Inst.*, 239, page 221 (1945) is that a rapid development is brought by the successive repetition of this procedure, thus giving a development with a high gamma.

While a sulfite is well known as one of the preservatives for a photographic developer composition, it is necessary to decrease the concentration of sulfite in

order to obtain more effective line and dot reproductions.

Infectious developer compositions of this kind, therefore, have poor stability as compared to common black and white photographic developers, and the life of the infectious developer composition is short. Consequently, when infectious developer compositions are continuously used, images having a low contrast and a high fringe are obtained because the development is not carried out rapidly. Accordingly, it has been proposed to add an anti-oxidant other than sulfite to improve the stability. In this attempt, it is already known to add ascorbic acid into an infectious developer composition solution (Great Britain Pat. No. 928,390). Ascorbic acid is, however, poor in stability and hence tends to be decomposed. Particularly, ascorbic acid tends to be decomposed when metal ions such as copper ions or iron ions are present in a developing solution. Further, it does not sufficiently stabilize the developer composition solution. Additionally, it has the drawbacks that the progress of development is slowed and that the dot quality is reduced when the ascorbic acid is added in a large amount.

An object of this invention is to provide a photographic developer composition for a high contrast photographic element useful for the graphic arts having an excellent stability unaccompanied by adverse influences on dot qualities.

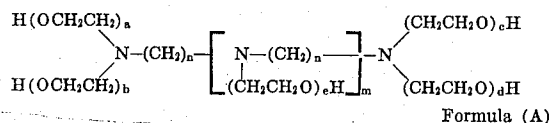
Another object of the invention is to provide an infectious developer composition which is easily controlled before and during development.

Still another object of the invention is to provide an infectious developer composition in which the amount of replenishment during development is reduced.

A further object of the invention to provide a photographic development process for the graphic arts capable of forming line and dot images having good qualities by using an infectious developer composition stable for a long period of time.

SUMMARY OF THE INVENTION

As the result of much research in order to attain such object, it has been found that the stability of the developer composition is markedly improved without any adverse influence upon the quality of images by adding at least one of the polyethoxy amino compound represented by the following formulae to an infectious developer composition.

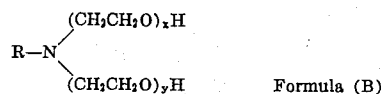


Formula (A)

wherein n range from 2 to 10,

m ranges from 0 to 6

$a + b + c + d + (e \times m)$ ranges from 5 to 200 with a, b, c, d , and e each representing an integer other than 0.



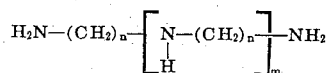
Formula (B)

wherein R represents an alkyl group of less than four carbon atoms with $x + y$ ranging from 3 to 100 or R represents an $-(\text{CH}_2\text{CH}_2\text{O})_z\text{H}$ group with $x + y + z$

ranging from 5 to 100, and x , y and z represent each an integer other than 0.

DETAILED DESCRIPTION OF THE INVENTION

The compounds represented by the above-described formula A used in the present invention can be produced by reacting commercially available compounds represented by the formula



(wherein n and m have the same meaning as set forth above), that is, polymers having at least two primary amino groups or secondary amino groups, with ethylene oxide in the desired molar amount (that is, such that sum of a , b , c , d and $e \times m$) using conventional techniques.

The compounds represented by the above-described formula B used in the present invention are produced by reacting primary amines or monoethanol amines with ethyleneoxide in the desired molar amount using conventional techniques.

In the following, representative compounds within the above-described formulae which can be used in the present invention are shown.

Compound 1:

Ethylene oxide addition product of ethylenediamine (addition mol number, i.e., the amount of ethyleneoxy units added: 30)

Compound 2:

Ethylene oxide addition product of hexamethylenediamine (addition mol number: 5)

Compound 3:

Ethylene oxide addition product of trimethylenediamine (addition mol number: 30)

Compound 4:

Ethylene oxide addition product of diethylenetriamine (addition mol number: 50)

Compound 5:

Ethylene oxide addition product of tetraethylenepentamine (addition mol number: 50)

Compound 6:

Ethylene oxide addition product of triethylenetetramine (addition mole number: 100)

Compound 7:

Ethylene oxide addition product of diethylenetriamine (addition mole number: 10)

Compound 8:

Ethylene oxide addition product of tetraethylenepentamine (addition mol number: 10)

Compound 9:

N,N-Di-polyoxyethylene ethylamine (addition mol number: 5)

Compound 10:

N,N,N-Tri-polyoxyethyleamine (addition mol number: 50)

Compound 11:

N,N-Di-polyoxyethylene butylamine (addition mol number: 80)

Use of the compounds of the present invention to photographic developer compositions is unknown, and particularly it is entirely unknown to improve the stability characteristics of developer compositions by adding to a developer of photographic materials for the graphic arts. As the result of examination of many com-

pounds, the present inventors have found the compounds represented by the above-described formulae improve the preservation characteristics of the developer. Why the preservation characteristics are improved by adding these compounds to the developer composition of photographic negatives for printing is not yet completely understood. But the preservability of the developer composition is improved in comparison with the known use of sodium sulfite or ascorbic acid etc. and the resulting photographic images obtained have little fringe and excellent halftone dots. Sodium sulfite and ascorbic acid have the disadvantage that the quality of the halftone dots deteriorates if these materials are added in a large amount. However, the compounds of the present invention do not deteriorate the quality of the halftone dots even though they are added in a large amount, as shown in examples herein-after.

When the compounds of the present invention are used in an infectious developer composition, a peculiar effect is obtained in that the halftone gradation becomes rich (soft) in addition to the preservability of the developer being improved without any deterioration of the quality of halftone dots. Accordingly, tone reproduction of an original is carried out more easily. Further, the development latitude (tolerance), that is the period during which optimum developing occurs, is prolonged and consequently it is easy to use.

The compounds of the present invention do not delay the proceeding of development. Rather they have a function of accelerating the proceeding of development when m is 1 or more and $a + b + c + d + e \times m$ is less than 10. By use of compounds which accelerate the proceeding of development, it is possible to carry out rapid treatment without elevating the temperature of the developer composition. Further, it is possible to obtain an infectious developer composition having a surprisingly long life and strong development activity by adding to an infectious developer composition of a low pH which has good preservability but poor development activity. In the present specification, "low pH" means that the pH is lower than that of the common infectious developer composition, and more specifically it means a pH 9.8 or so.

An infectious developer composition, in use, is basically composed of a dihydroxybenzene (developing agent), an alkali, a small amount of sulfite and, if necessary, a sulfite ion buffer. The infectious developer composition of the invention further contains the aforesaid polyethoxy amino compound.

Dihydroxybenzenes are known in the art and can be easily selected by one skilled in the art. Typical examples of these compounds are hydroquinone, chlorohydroquinone, bromohydroquinone, isopropylhydroquinone, toluhydroquinone, methylhydroquinone, 2, 3-dichlorohydroquinone, 2,5-dimethylhydroquinone, etc. As developing agents, hydroquinone is preferably used. These developing agents are used singly or in combination. A suitable amount of the developing agent to be added ranges from about 5 to 50 g., preferably about 10 to 30 g., per 1 liter of the developer composition.

A sulfite ion buffer can be used in such an amount that concentration of sulfite is maintained at a low level in the developer composition. Examples of such buffers are an aldehyde-alkali metal hydrogen sulfite addition product such as formalin-sodium hydrogen sulfite, a

ketone-alkali metal hydrogen sulfite addition product such as acetone-sodium hydrogen sulfite addition product, and a carbonylbisulfiteamine condensation product such as sodium bis-(2-hydroxyethyl)-aminomethane sulfonate. The sulfite ion buffer is not limited to the above examples and each ingredient of the addition product or condensation product may be added to the developer. The amount of the sulfite ion buffer which is added can range from about 13 to 130 g., preferably 30 to 60 g. per one liter of the developer composition.

An alkali is added to adjust the developer composition to an alkaline condition preferably to a pH higher than 8, more preferably to a pH of 9 to 11. Accordingly, the addition amount and kind of additive can be freely selected and is not limited to the above examples.

The developer solution can contain further a pH buffer agent, such as an alkanolamine, a water-soluble acid (e.g., acetic acid, boric acid), an alkali (e.g., sodium hydroxide) or a salt (e.g., sodium carbonate). Further, it may contain an alkali metal halide as a development controlling agent. Also, it may contain in some cases an organic anti-fogging agent (e.g., benzotriazole, 1-phenyl-5-mercapto-tetrazole), a polyalkylene oxide, an amine, and an organic solvent (e.g., triethylene glycol, dimethylformamide, methanol, cellosolve) in an amount of not more than 300 ml per 1 liter of the developer solution.

As described above, a characteristic of the infectious developer solution is that the concentration of free sulfite is low. For this purpose a sulfite ion buffer material such as formaldehyde-sodium bisulfite adduct is generally employed.

In general, the concentration of free sulfite ions is controlled by the addition of an alkali metal sulfite such as sodium sulfite in an amount of not more than 5 g per 1 liter of the developer solution as well as a sulfite ion buffer agent. Sulfite is generally added in an amount of not more than 3 g per liter of the developer solution, and thereby the stability of the developer solution is slightly improved, although the dot quality is more or less reduced. However, as described above, this degree of the stability is generally not satisfactory. Although the compounds of the present invention improve the inherently poor stability of an infectious developer solution which does not contain an alkali sulfite other than a sulfite ion buffer agent such as a formaldehyde-sodium bisulfite adduct to a certain extent, they remarkably improve the stability of an infectious developer solution which contains both an alkali sulfite in an amount of not more than 5 g per 1 liter of the developer solution (0.005 - 0.05 mole of free sulfite) and a sulfite ion buffer agent. That is to say, the compounds of the present invention exert an effect even in a developer solution which does not contain a free sulfite (e.g., a developer solution which does not contain a sulfite other than formaldehyde-bisulfite adduct), but this effect is very small. Accordingly, from a practical standpoint the present invention can be employed best in a developer solution containing a small amount of free sulfite. A single compound of this invention or a combination of two or more compounds of this invention can be used. The amount of the compounds of the present invention added to a developer solution varies according to the composition of the developing solution and the kind of the compounds used, but the amount em-

ployed generally is in the range of from 0.1 g to 100 g per 1 liter of the developing solution, more preferably from 0.1 g to 60 g per 1 liter of the developer solution.

When the developing compounds are processed prior to use so that they may be readily used as developer solutions on mixing with water or dissolving in water, that is, when they are in the form of liquid or powdered developer compositions, it is effective to incorporate the compounds of the present invention into the developer preparations beforehand. When liquid preparations are used, it is particularly effective to add the compounds of the present invention since they improve remarkably the stability of the liquid preparations. Liquid preparations generally are not known to have a good stability, and therefore it is difficult to obtain a stable developer composition, since the liquid preparations can not contain a large amount of salts (e.g., carbonylbisulfite) due to the characteristics of liquid preparations. Therefore, it is particularly desirable to use the hydrazine compounds of the present invention in liquid preparations.

A general liquid preparation comprises two liquid compositions, that is, a liquid component containing the developing agent and a liquid component containing an alkali. The compounds of the present invention may be incorporated into any such components, but it is particularly effective to add them to the component containing the developing agent. With this treatment, a liquid developing agent having an excellent stability and an infectious developer solution prepared by dilution of said liquid developing agent having a markedly excellent stability, can be obtained.

As solvents for the liquid developing agent, there may be used solvents such as water, benzyl alcohol, ethylene glycol, diethylene glycol, triethylene glycol, glacial acetic acid or a combination of these solvents. Alternatively, it is possible to improve the stability of the developer solution by adding the compounds of the present invention in the course of development or after development of the photographic materials for printing.

Light-sensitive materials for printing, used in the present invention, include common silver halide emulsions (e.g., silver chloride emulsions, silver chlorobromide emulsions, silver chloriodobromide emulsions). Particularly, silver chlorobromide emulsions and silver chloriodobromide emulsions, containing not less than about 50 mole percent of silver chloride, are suitable for the present invention. As silver halide-dispersing agents containing these light-sensitive materials, hydrophilic colloidal substances, such as gelatin or gelatin derivatives (e.g., collodion), hydroxyethylcellulose, carboxymethylcellulose; water-soluble starches (e.g., dextrin, alkali starch); or hydrophilic polymers (e.g., polyvinyl alcohols, polyvinyl pyrrolidines, polyacrylamides, polystyrenesulfonic acids) can be used. These light-sensitive materials may contain additionally hydrophobic polymers such as polyacrylates, and gelatin-plasticizers such as glycerin or trimethanolpropane.

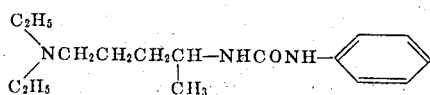
The emulsions used in these light-sensitive materials may be sensitized using various techniques either when the materials are manufactured or when the materials are applied. For example, they may be chemically sensitized by methods well known in the art, for example, with sodium thiosulfate, alkylthiourea, gold compounds such as complexes of monovalent gold and thi-

oceanic acid, or mixtures of these. Further, the emulsions may contain heavy metals such as platinum, palladium, iridium, rhodium or cadmium. In addition, the emulsions may be panchromatically or orthochromatically sensitized with color-sensitizers such as cyanine dyes or merocyanine dyes. Yet further, the emulsions may contain dot quality-improving agents such as polyalkyleneoxides and amine compounds (U.S. Pat. No. 3,288,612, German Specification OLS 1,932,882, U.S. Pat. No. 3,345,175) and sodium benzenethiosulfate, benzenetriazole and 1,3,3a, 7-tetrazaindene derivatives (U.S. Pat. No. 3,375,114 or U.S. Pat. No. 3,333,959). The emulsions may be hardened with formaldehyde, resorcyaldehyde, dimethylol urea, 2, 4-dichloro-6-hydroxy-1,3,5-triazine (U.S. Pat. No. 3,325,287) or mucochloric acid, or they may contain surface-active agents such as saponin in order to facilitate the application of the emulsions. The emulsions may further contain agents which improve the progress of development such as 3-pyrazolidone derivatives or pyrazolone derivatives. Further, the emulsion may contain development-accelerating agents such as quaternary ammonium salts or cationic surface-active agents. The supports used in the present invention are not limited, and glass, cellulose acetate, polystyrene, polycarbonate, polyethylene terephthalate and the like may be used.

The present invention will now be illustrated in greater detail by the following examples.

EXAMPLE 1

A lithofilm was produced by carrying out gold sensitization and sulfur sensitization of a silver halide emulsion comprising 75 mol percent silver chloride, 0.2 mol percent silver iodide and the balance of silver bromide, carrying out optical sensitization using 3-carboxymethyl-5-[2-(3-ethylthiazolinyldene)ethylidene]rhodamine, adding polyoxyethylene nonylphenyl ether containing 50 ethylene oxide groups and a development accelerating agent



described in Japanese Patent Publication No. 23465/65, adding mucochloric acid, mixing with polybutylmethacrylate polymer, and applying the emulsion to a support. After photographing using an exposing wedge for sensitometry on this litho film through a 150 line magneta contact screen, the film was developed with using five kinds of developer compositions having the following composition at 27°C.

Developer Composition A

Sodium Carbonate (monohydrate)	50 g
Formaldehyde-Sodium Hydrogen Sulfite Addition Product	45 g
Potassium Bromide	2 g
Hydroquinone	18 g
Sodium Sulfite	2 g
Water to make	1 liter

Developer Composition B

Developer Composition B was produced by adding 2 g/l. of Compound 1 of this invention to Developer Composition A (the pH was the same as in Developer Composition A).

Developer Composition C

Developer Composition C was produced by adding 40 g/l. of Compound 2 of the present invention to Developer Composition A (the pH was the same as in Developer Composition A).

Developer Composition D

Developer Composition D was produced by adding 5 g/l. of sodium sulfite to Developer A (the pH was the same as in Developer Composition A).

Developer Composition E

Developer Composition E was produced by adding 1 g/l. of ascorbic acid to Developer Composition A (the pH was the same as in Developer Composition A).

The results obtained using the above are shown in Table 1.

Table 1

Developer Composition	Additive	Development Time (second)	Halftone Dot Quality	Halftone Gradation	Sensitivity	
					Fresh Liquid	Aerated Liquid
A	—	90	a	15	100	36
B	Compound 1	90	a	17	100	80
C	Compound 2	90	a	16	100	85
D	Sodium Sulfate	120	c	14	100	60
E	Ascorbic Acid	120	a	15	100	55

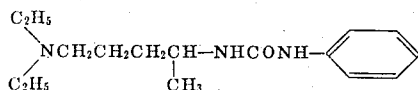
The Development Time is that time for reaching the sensitivity obtained on development using Developer Composition A for 90 seconds (this sensitivity is set for 100). The Halftone Dot Quality was evaluated and the results are shown in Table 1 using an a, b, and c ranking system, in which a means good, b means somewhat good and c means bad. The Halftone Gradation shows number of stages of from 10 percent halftone dot to 90 percent halftone dot. The aerated liquid means a developer composition which was subjected to deterioration by contacting 500 ml of the developer composition in a 20 cm × 25 cm developing vat with air for 5 hours.

As can be seen from the results contained in the above table, the compounds of the present invention improve the stability of the developer compositions without having a large influence upon photographic properties and have the function of softening the halftone gradation.

EXAMPLE 2

Using a commercially available litho film comprising a silver halide emulsion containing 75 mole percent of silver chloride and 0.2 mole percent of silver iodide, the remainder of the halide being silver bromide, which was subjected to gold sensitization and sulfur sensitization, then photosensitized with 3-carboxymethyl-5-[2-

(3-ethylthiazolinilidene)ethylidene]rhodonine, then, thereto were added a polyoxyethylene nonylphenylether containing 50 ethyleneoxide groups, the development-accelerating agent



described in the Japan Patent Publication No. 23465/65, mucochloric acid and polybutylmethacrylate and coated on a film base, an exposing wedge for sensitometry was photographed through a 150 line magenta contact screen. Then the film was developed using developer compositions having the following composition in an automatic developing apparatus for plate making (at 27°C; development time: 100 seconds).

Developer Composition F

Solution I:	
Water	60 ml
Triethylene Glycol	30 ml
Formaldehyde-Sodium Hydrogen	
Sulfite Addition Product	45 g
Sodium Sulfite	1 g
Hydroquinone	16 g
Water to make	125 ml

Solution II:	
Water	100 ml
Sodium Carbonate (monohydrate)	30 g
Sodium Hydroxide	5 g
Boric Acid	3 g
Sodium Bromide	2 g
Water to make	125 ml

On use, Solution I is added to 750 ml of water and Solution II is then added thereto to make 1 liter.

Developer Compositions G, H and I were produced by adding the following compounds respectively to Developer Composition F (the pH of the resulting developer compositions were the same as in Developer Composition F).

The results obtained are shown in Table 2.

Table 2

Developer Composition	Additive	Amount (g/l.)	Halftone Dot Quality	Halftone Gradation	Sensitivity	
					Fresh Liquid	Aerated Liquid
F	—	—	a	16	100	30
G	Compound 3	5	a	18	100	97
H	Compound 4	20	a	17	100	100
I	Compound 10	13	a	18	100	95

The Halftone Dot Quality and the Halftone Gradation are indicated in the same manner as in Example 1. The aerated liquid is a developer composition which was subjected to deterioration by leaving the developer composition for two days in an automatic developing apparatus. Usually, in the developer compositions for photographic negatives for printing, any deterioration of the sensitivity is corrected by adding a supplementary solution as is required. However, the effect of the compounds of the present invention is surprisingly large and an addition of a supplementary solution is not required.

EXAMPLE 3.

The same effect is obtained with using the following solution as the supplemental solution for developer F in Example 2.

Supplement Solution	
Triethylene Glycol	40 ml
Formaldehyde-Sodium Sulfite	
Addition Product	45 g
Sodium Sulfite	1 g
Sodium Carbonate (monohydrate)	25 g
Hydroquinone	18 g
Boric Acid	4 g
Compound 5	50 g
Triethanol Amine	10 ml
Water to make	1 liter

EXAMPLE 4.

With using a litho film as described in Example 1, an exposing wedge for sensitometry was photographed through a 150 line magenta contact screen. Then, the film was developed using four kinds of developers having the following compositions at 27°C.

Developer Composition	
Sodium Carbonate (monohydrate)	50 g
Formaldehyde-Sodium Hydrogen	
Sulfite Addition Product	45 g
Potassium Bromide	2 g
Hydroquinone	18 g
Sodium Sulfite	2 g
Sodium Hydroxide or Acetic Acid	Amount necessary to control pH.
Water to make	1 liter

Developer Composition J was prepared using the above-described composition and adjusting the pH to 10.30.

Developer Composition K was prepared using the above-described composition and adjusting the pH to 9.80.

Developer Composition L was prepared by adding 0.5 g/l. of Compound 7 to the above-described composition and adjusting the pH to 9.80.

Developer Composition M was prepared by adding 0.1 g/l. of Compound 8 and 20 g/l. of Compound 6 to the above-described composition and adjusting the pH to 9.80.

The results obtained are shown in Table 3.

Table 3

Developer Composition	Additive	pH	Development Time	Halftone Dot Quality	Sensitivity	
					Fresh Liquid	Aerated Liquid
			(second)			(24 hours)
J	—	10.30	90	a	100	10
K	—	9.80	240	a	100	50
L	Compound 7	9.80	90	a	100	98
M	Compound 8	9.80	90	a	100	100

The aerated liquid is a developer composition which was subjected to deterioration by contacting 500 ml of the developer composition in a 20 cm × 25 cm developing vat with air for 24 hours.

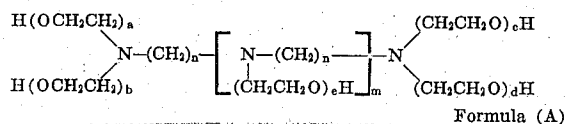
In developer compositions having a low pH, although the preservability is excellent, the development time is markedly long. However, when the compounds of the present invention having a development accelerating property are used together, the stability is markedly improved without delaying the development time.

EXAMPLE 5.

A film having the same properties can be obtained by developing using a developer composition having a pH of 10.30 which is prepared by adding 0.15g/l. of Compound 8 to Developer Composition F using an automatic developing apparatus for plate making for 35 seconds (temperature of development: 27°C) as was obtained by developing with Developer Composition F for 90 seconds.

What is claimed is:

1. An infectious photolithographic developer composition for producing photographic materials for the graphic arts comprising a hydroquinone or hydroquinone derivative developing agent, 0.005 to 0.05 mol free sulfite per liter, and at least one polyethoxyamino compound represented by the following formula A:



wherein n ranges from 2 to 10;

m ranges from 0 to 6; and

$a + b + c + d + e \times m$ ranges from 5 to 200 with a , b , c , d and e each representing an interger other than 0.

2. The developer composition of claim 1, wherein said composition additionally contains an aldehyde-alkali metal bisulfite adduct, a ketone-alkali metal bisulfite adduct or a combination thereof.

3. The developer composition of claim 2, wherein said composition contains formaldehyde-sodium bisulfite adduct.

4. The developer composition of claim 1, wherein said developing agent is hydroquinone, chlorohydroquinone, bromohydroquinone, isopropylhydroquinone, toluhydroquinone, methylhydroquinone, 2,3-dichlorohydroquinone, or 2,5-dimethylhydroquinone.

5. The developer composition of claim 4, wherein said developing agent is hydroquinone.

6. The developer composition of claim 1, wherein said polyethoxy amino compound is present at a level ranging from 0.1 g to 100 g per liter of the developer composition and wherein said developing agent is present at a level ranging from 5 to 50 g per liter of developer composition.

7. A method for producing a photographic line of half-tone reproduction in the graphic arts comprising exposing a high contrast photographic element and developing said exposed element in the developer composition of claim 1.

8. The method of claim 7, wherein said composition additionally contains a aldehyde-alkali metal bisulfite adduct, a ketone-alkali metal bisulfite adduct or a combination thereof.

9. The method of claim 8, wherein said composition contains formaldehyde-sodium busulfite adduct.

10. The method of claim 7, wherein said developing agent is hydroquinone, chlorohydroquinone, bromohydroquinone, isopropylhydroquinone, toluhydroquinone, methylhydroquinone, 2,3-dichlorohydroquinone, or 2,5-dimethylhydroquinone.

11. The method of claim 10, wherein said developing agent is hydroquinone.

12. The method of claim 7, wherein said polyethoxy amino compound is present at a level ranging from 0.1 g to 100 g per liter of developer composition and wherein said developing agent is present at a level ranging from 5 to 50 g per liter of developer composition.

13. The developer composition of claim 1, wherein said compound is an ethylene oxide addition product of ethylenediamine having an addition mol number of 30.

14. The developer composition of claim 1, wherein said compound is an ethylene oxide addition product of hexamethylenediamine having an addition mol number of 5.

15. The developer composition of claim 1, wherein said compound is an ethylene oxide addition product of trimethylenediamine having an addition mol number of 30.

16. The developer composition of claim 1, wherein said compound is an ethylene oxide addition product of diethylenetriamine having an addition mol number of 50.

17. The developer composition of claim 1, wherein said compound is an ethylene oxide addition product of tetraethylenepentamine having an addition mol number of 50.

18. The developer composition of claim 1, wherein said compound is a methylene oxide addition product of triethylenetetramine having an addition mol number of 100.

19. The developer composition of claim 1, wherein said compound is an ethylene oxide addition product of diethylenetriamine having an addition mol number of 10.

20. The developer composition of claim 1, wherein said compound is an ethylene oxide addition product of tetraethylenepentamine having an addition mol number of 10.